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(21) International Application Number: <b>PCT/US93/08471</b> (22) International Filing Date: <b>9 September 1993 (09.09.93)</b> (30) Priority data: 07/943,844                      11 September 1992 (11.09.92) <b>US</b> (71) Applicant: <b>CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US];</b> Post Office Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventors: <b>CALLIS, Glenn, E. ;</b> 1089 Walnut Avenue, Walnut Creek, CA 94598 (US). <b>SABOURIN, Edward, T. ;</b> 11 Avichi Knoll, Novato, CA 94947 (US). (74) Agents: <b>CAROLI, Claude, J. et al.;</b> Chevron Corporation, Law Department, Post Office Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: <b>AU, CA, JP,</b> European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: <b>FUEL COMPOSITION FOR TWO-CYCLE ENGINES</b>			
(57) Abstract			
<p>A fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a base oil of lubricating viscosity and an additive formulation comprising (1) a molybdenum/sulfur complex of a basic nitrogen compound, (2) a carboxylic acid amide, and (3) a succinimide.</p>			
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## 01 FUEL COMPOSITION FOR TWO-CYCLE ENGINES

02

03 BACKGROUND OF THE INVENTION

04

05 The present invention relates to a fuel composition for  
06 two-cycle internal combustion engines which comprises a  
07 major amount of fuel boiling in the gasoline range and a  
08 minor amount of a lubricant composition comprising a  
09 lubricating oil and an additive formulation containing a  
10 molybdenum/sulfur complex of a basic nitrogen compound.

11

12 Over the past several decades the use of spark-ignited  
13 two-cycle (two-stroke) internal combustion engines including  
14 rotary engines such as those of the Wankel type has steadily  
15 increased. They are presently found in power lawn mowers  
16 and other power-operated garden equipment, power chain saws,  
17 pumps, electrical generators, marine outboard engines,  
18 snowmobiles, motorcycles, and the like.

19

20 The increasing use of two-cycle engines coupled with  
21 increasing severity of the conditions in which they have  
22 operated has led to an increasing demand for oils to  
23 adequately lubricate such engines. Among the problems  
24 associated with lubrication of two-cycle engines are piston  
25 ring sticking, rusting, lubrication failure of connecting  
26 rods and main bearings and the general formation on the  
27 engine's interior surface of carbon and varnish deposits.  
28 The formation of varnish is a particularly vexatious problem  
29 since the build-up of varnish on piston and cylinder walls  
30 is believed to ultimately result in ring sticking which  
31 leads to failure of the sealing function of piston rings.  
32 Such seal failure causes loss of cylinder compression which  
33 is particularly damaging in two-cycle engines because they  
34 depend on suction to draw the new fuel charge into the

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01 exhausted cylinder. Thus, ring sticking can lead to  
02 deterioration in engine performance, and unnecessary  
03 consumption of fuel and/or lubricant. Spark plug fouling  
04 and engine port plugging problems also occur in two-cycle  
05 engines.

06  
07 A variety of compounds have been proposed as additives for  
08 fuel-lubricating oil mixtures to be used in two-cycle  
09 internal combustion engines. For example, U.S. Patent  
10 No. 4,708,809 to Davis discloses a lubricant composition for  
11 two-cycle engines comprising a major amount of an oil of  
12 lubricating viscosity and a minor amount of at least one  
13 alkyl phenol having at least one hydrocarbon-based group of  
14 at least 10 aliphatic carbon atoms. Preferably, such  
15 lubricant composition will also contain a detergent-  
16 dispersant additive selected from (i) a neutral or basic  
17 metal salt of an organic sulfur acid, phenol or carboxylic  
18 acid, (ii) a hydrocarbyl-substituted amine, (iii) an  
19 acylated, nitrogen-containing compound having a substituent  
20 of at least 10 aliphatic carbon atoms, (iv) a  
21 nitrogen-containing condensate of a phenol, aldehyde and  
22 amino compound, and (v) an ester of a substituted  
23 polycarboxylic acid.

24  
25 U.S. Patent No. 4,724,091 to Davis discloses a lubricant  
26 composition for two-cycle engines comprising a major amount  
27 of an oil of lubricating viscosity and a minor amount of a  
28 mixture of at least one alkyl phenol and at least one amino  
29 phenol, each phenol having at least one hydrocarbon-based  
30 group of at least about 10 aliphatic carbon atoms.  
31 Preferably, this composition will additionally contain a  
32 detergent-dispersant additive.

33  
34

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01 U.S. Patent No. 4,740,321 to Davis et al. discloses a  
02 lubricant composition for two-cycle engines comprising a  
03 major amount of an oil of lubricating viscosity and a minor  
04 amount of at least one sulfurized alkyl phenol or metal salt  
05 thereof having at least one hydrocarbon-based group of at  
06 least 10 aliphatic carbon atoms. This lubricant composition  
07 will also preferably contain a detergent-dispersant  
08 additive.

09

10 U.S. Patent No. 4,705,643 to Nemo discloses a lubricating  
11 oil composition for two-cycle engines comprising a  
12 lubricating oil and an ashless detergent additive which is  
13 the hydrolyzed reaction product of an aliphatic branched  
14 chain carboxylic acid of 16 to 20 carbon atoms and a  
15 polyamine of at least 3 amine groups. Preferably, the  
16 ashless detergent additive is the hydrolyzed reaction  
17 product of isostearic acid and tetraethylenepentamine.

18

19 U.S. Patent No. 4,994,196 to Kagaya et al. discloses a  
20 two-cycle engine oil composition comprising a base oil and a  
21 calcium phenate detergent additive, wherein the base oil is  
22 a mixture of (a) a copolymer of an alpha-olefin with an  
23 ester of a dicarboxylic acid and (b) an ester of  
24 pentaerythritol and a fatty acid.

25

26 U.S. Patent No. 3,888,776 to Silverstein discloses a  
27 two-cycle engine lubricant which comprises a major amount of  
28 a polypropylene glycol and minor amounts of a sulfurized  
29 oxymolybdenum organophosphorodithioate, a finely divided  
30 molybdenum disulfide and a halogenated hydrocarbon  
31 detergent, such as 1,1,1-trichloroethylene,  
32 orthodichlorobenzene, perchlorinated biphenyl, and the like.

33

34

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01 Molybdenum/sulfur complexes of basic nitrogen compounds have  
02 previously been described in the art as useful antioxidant  
03 additives for lubricant compositions finding application,  
04 for example, as crosshead diesel engine lubricants,  
05 automobile and railroad crankcase lubricants, lubricants for  
06 heavy machinery, greases for bearings, and the like.

07  
08 For example, U.S. Patent No. 4,263,152 to King et al.  
09 discloses an antioxidant additive for lubricating oils which  
10 is prepared by combining an acidic molybdenum compound, a  
11 polar promoter, a basic nitrogen-containing compound and a  
12 sulfur source to form a molybdenum and sulfur-containing  
13 complex. Similar molybdenum-containing antioxidant  
14 additives are disclosed in U.S. Patent Nos. 4,285,822;  
15 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195; and  
16 4,259,194. However, none of these patents teaches or  
17 appreciates the use of such antioxidant additives, or  
18 lubricating oils containing such additives, in admixture  
19 with fuels in two-cycle engines. Furthermore, none of these  
20 patents teaches or appreciates that such antioxidant  
21 additives would be effective deposit control agents or would  
22 reduce piston sticking when utilized in fuel-lubricating oil  
23 mixtures in two-cycle engines.

24  
25 Moreover, as taught in the aforementioned U.S. Patent  
26 No. 4,708,809, the unique problems and techniques associated  
27 with the lubrication of two-cycle engines has led to the  
28 recognition by those skilled in the art of two-cycle engine  
29 lubricants as a distinct lubricant type.

30  
31 Accordingly, the present invention is directed to minimizing  
32 the problems of varnish build-up and ring sticking in  
33 two-cycle engines through the provision of effective  
34 additives for fuel-lubricating oil combinations which

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01 eliminate or reduce two-cycle engine varnish deposits and  
02 piston ring seal failure.

03

04 SUMMARY OF THE INVENTION

05

06 The present invention provides a fuel composition for  
07 two-cycle engines comprising a major amount of fuel boiling  
08 in the gasoline range and a minor amount of a lubricant  
09 composition comprising:

10

11 (A) a major amount of a base oil of lubricating viscosity,  
12 and

13

14 (B) a minor amount of an additive formulation comprising:

15

16 (1) a sulfurized molybdenum-containing composition  
17 prepared by (i) reacting an acidic molybdenum  
18 compound and a basic nitrogen compound selected  
19 from the group consisting of a succinimide, a  
20 carboxylic acid amide, a hydrocarbyl monoamine, a  
21 hydrocarbyl polyamine, a Mannich base, a  
22 phosphoramidate, a thiophosphoramidate, a  
23 phosphonamidate, a dispersant viscosity index  
24 improver, or a mixture thereof, in the presence of  
25 a polar promoter, to form a molybdenum complex  
26 wherein from 0.01 to 2 atoms of molybdenum are  
27 present per basic nitrogen atom, and the promoter  
28 is present in the ratio of 0.01 to 50 moles of  
29 polar promoter per mole of molybdenum; and  
30 (ii) reacting the molybdenum complex with a  
31 sulfur-containing compound in an amount sufficient  
32 to provide about 1.5 to 4.0 atoms of sulfur per  
33 atom of molybdenum, to thereby form a sulfur- and  
34 molybdenum-containing composition,

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01           (2) a carboxylic acid amide, and

02  
03           (3) a succinimide.

04  
05   Among other factors, the present invention is based upon the  
06   unexpected discovery that additive formulations containing a  
07   molybdenum/sulfur complex of a basic nitrogen compound, plus  
08   a carboxylic acid amide and a succinimide are surprisingly  
09   effective agents for deposit control and reduction of piston  
10   ring sticking when combined in fuel-lubricating oil mixtures  
11   in two-cycle engines.

12  
13                   DETAILED DESCRIPTION OF THE INVENTION

14  
15   The fuel composition of the present invention will comprise  
16   a major amount of fuel boiling in the gasoline range and a  
17   minor amount of a lubricant composition comprising a base  
18   oil of lubricating viscosity and an additive formulation  
19   containing (1) a sulfurized molybdenum-containing  
20   composition, (2) a carboxylic acid amide, and (3) a  
21   succinimide.

22  
23   The sulfurized molybdenum-containing composition employed in  
24   the present invention may be generally characterized as a  
25   molybdenum/sulfur complex of a basic nitrogen compound.  
26   Such molybdenum/sulfur complexes are known in the art and  
27   are described, for example, in U.S. Patent No. 4,263,152 to  
28   King et al., the disclosure of which is hereby incorporated  
29   by reference.

30  
31   The precise molecular formula of the molybdenum compositions  
32   employed in this invention is not known with certainty;  
33   however, they are believed to be compounds in which  
34   molybdenum, whose valences are satisfied with atoms of



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01 oxygen or sulfur, is either complexed by, or the salt of,  
02 one or more nitrogen atoms of the basic nitrogen containing  
03 compound used in the preparation of these compositions.  
04

05 The molybdenum compounds used to prepare the  
06 molybdenum/sulfur complexes employed in this invention are  
07 acidic molybdenum compounds. By acidic is meant that the  
08 molybdenum compounds will react with a basic nitrogen  
09 compound as measured by ASTM test D-664 or D-2896 titration  
10 procedure. Typically these molybdenum compounds are  
11 hexavalent and are represented by the following  
12 compositions: molybdic acid, ammonium molybdate, sodium  
13 molybdate, potassium molybdate and other alkaline metal  
14 molybdates and other molybdenum salts such as hydrogen  
15 salts, e.g., hydrogen sodium molybdate,  $\text{MoOCl}_4$ ,  $\text{MoO}_2\text{Br}_2$ ,  
16  $\text{Mo}_2\text{O}_3\text{Cl}_6$ , molybdenum trioxide or similar acidic molybdenum  
17 compounds. Preferred acidic molybdenum compounds are  
18 molybdic acid, ammonium molybdate, and alkali metal  
19 molybdates. Particularly preferred are molybdic acid and  
20 ammonium molybdate.  
21

22 The basic nitrogen compound used to prepare the  
23 molybdenum/sulfur complexes must have a basic nitrogen  
24 content as measured by ASTM D-664 or D-2896. It is  
25 preferably oil-soluble. Typical of such compositions are  
26 succinimides, carboxylic acid amides, hydrocarbyl  
27 monoamines, hydrocarbon polyamines, Mannich bases,  
28 phosphoramides, thiophosphoramides, phosphoramides,  
29 dispersant viscosity index improvers, and mixtures thereof.  
30 These basic nitrogen-containing compounds are described  
31 below (keeping in mind the reservation that each must have  
32 at least one basic nitrogen). Any of the  
33 nitrogen-containing compositions may be after-treated with,  
34

01 e.g., boron, using procedures well known in the art so long  
02 as the compositions continue to contain basic nitrogen.  
03 These after-treatments are particularly applicable to  
04 succinimides and Mannich base compositions.  
05

06 The mono and polysuccinimides that can be used to prepare  
07 the molybdenum/sulfur complexes described herein are  
08 disclosed in numerous references and are well known in the  
09 art. Certain fundamental types of succinimides and the  
10 related materials encompassed by the term of art  
11 "succinimide" are taught in U.S. Patent Nos. 3,219,666;  
12 3,172,892; and 3,272,746, the disclosures of which are  
13 hereby incorporated by reference. The term "succinimide" is  
14 understood in the art to include many of the amide, imide,  
15 and amidine species which may also be formed. The  
16 predominant product however is a succinimide and this term  
17 has been generally accepted as meaning the product of a  
18 reaction of an alkenyl substituted succinic acid or  
19 anhydride with a nitrogen-containing compound. Preferred  
20 succinimides, because of their commercial availability, are  
21 those succinimides prepared from a hydrocarbyl succinic  
22 anhydride, wherein the hydrocarbyl group contains from about  
23 24 to about 350 carbon atoms, and an ethylene amine, said  
24 ethylene amines being especially characterized by ethylene  
25 diamine, diethylene triamine, triethylene tetramine, and  
26 tetraethylene pentamine. Particularly preferred are those  
27 succinimides prepared from polyisobutenyl succinic anhydride  
28 of 70 to 128 carbon atoms and tetraethylene pentamine or  
29 triethylene tetramine or mixtures thereof.  
30

31 Also included within the term "succinimide" are the  
32 cooligomers of a hydrocarbyl succinic acid or anhydride and  
33 a poly secondary amine containing at least one tertiary  
34 amino nitrogen in addition to two or more secondary amino

01 groups. Ordinarily this composition has between 1,500 and  
02 50,000 average molecular weight. A typical compound would  
03 be that prepared by reacting polyisobutenyl succinic  
04 anhydride and ethylene dipiperazine.

05

06 Carboxylic acid amide compositions are also suitable  
07 starting materials for preparing the molybdenum/sulfur  
08 complexes employed in this invention. Typical of such  
09 compounds are those disclosed in U.S. Patent No. 3,405,064,  
10 the disclosure of which is hereby incorporated by reference.  
11 These compositions are ordinarily prepared by reacting a  
12 carboxylic acid or anhydride or ester thereof, having at  
13 least 12 to about 350 aliphatic carbon atoms in the  
14 principal aliphatic chain and, if desired, having sufficient  
15 pendant aliphatic groups to render the molecule oil soluble  
16 with an amine or a hydrocarbyl polyamine, such as an  
17 ethylene amine, to give a mono or polycarboxylic acid amide.  
18 Preferred are those amides prepared from (1) a carboxylic  
19 acid of the formula  $R^2COOH$ , where  $R^2$  is  $C_{12-20}$  alkyl or a  
20 mixture of this acid with a polyisobutenyl carboxylic acid  
21 in which the polyisobutenyl group contains from 72 to  
22 128 carbon atoms and (2) an ethylene amine, especially  
23 triethylene tetramine or tetraethylene pentamine or mixtures  
24 thereof.

25

26 Another class of compounds which are useful in this  
27 invention are hydrocarbyl monoamines and hydrocarbyl  
28 polyamines, preferably of the type disclosed in U.S. Patent  
29 No. 3,574,576, the disclosure of which is hereby  
30 incorporated by reference. The hydrocarbyl group, which is  
31 preferably alkyl, or olefinic having one or two sites of  
32 unsaturation, usually contains from 9 to 350, preferably  
33 from 20 to 200 carbon atoms. Particularly preferred

34

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01 hydrocarbyl polyamines are those which are derived, e.g., by  
02 reacting polyisobutenyl chloride and a polyalkylene  
03 polyamine, such as an ethylene amine, e.g., ethylene  
04 diamine, diethylene triamine, tetraethylene pentamine,  
05 2-aminoethylpiperazine, 1,3-propylene diamine,  
06 1,2-propylenediamine, and the like.

07  
08 Another class of compounds useful for supplying basic  
09 nitrogen are the Mannich base compositions. These  
10 compositions are prepared from a phenol or C<sub>9-200</sub>  
11 alkylphenol, an aldehyde, such as formaldehyde or  
12 formaldehyde precursor such as paraformaldehyde, and an  
13 amine compound. The amine may be a mono or polyamine and  
14 typical compositions are prepared from an alkylamine, such  
15 as methylamine or an ethylene amine, such as, diethylene  
16 triamine, or tetraethylene pentamine, and the like. The  
17 phenolic material may be sulfurized and preferably is  
18 dodecylphenol or a C<sub>80-100</sub> alkylphenol. Typical Mannich  
19 bases which can be used in this invention are disclosed in  
20 U.S. Patent No. 4,157,309 and U.S. Patent Nos. 3,649,229;  
21 3,368,972; and 3,539,663, the disclosures of which are  
22 hereby incorporated by reference. The last referenced  
23 patent discloses Mannich bases prepared by reacting an  
24 alkylphenol having at least 50 carbon atoms, preferably 50  
25 to 200 carbon atoms with formaldehyde and an alkylene  
26 polyamine  $\text{HN}(\text{ANH})_n\text{H}$  where A is a saturated divalent alkyl  
27 hydrocarbon of 2 to 6 carbon atoms and n is 1-10 and where  
28 the condensation product of said alkylene polyamine may be  
29 further reacted with urea or thiourea. The utility of these  
30 Mannich bases as starting materials for preparing  
31 lubricating oil additives can often be significantly  
32 improved by treating the Mannich base using conventional  
33 techniques to introduce boron into the composition.  
34

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01 Another class of composition useful for preparing the  
02 molybdenum/sulfur complexes employed in this invention are  
03 the phosphoramides and phosphonamides such as those  
04 disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157, the  
05 disclosures of which are hereby incorporated by reference.  
06 These compositions may be prepared by forming a phosphorus  
07 compound having at least one P-N bond. They can be  
08 prepared, for example, by reacting phosphorus oxychloride  
09 with a hydrocarbyl diol in the presence of a monoamine or by  
10 reacting phosphorus oxychloride with a difunctional  
11 secondary amine and a mono-functional amine.

12 Thiophosphoramides can be prepared by reacting an  
13 unsaturated hydrocarbon compound containing from 2 to 450 or  
14 more carbon atoms, such as polyethylene, polyisobutylene,  
15 polypropylene, ethylene, 1-hexene, 1,3-hexadiene,  
16 isobutylene, 4-methyl-1-pentene, and the like, with  
17 phosphorus pentasulfide and a nitrogen-containing compound  
18 as defined above, particularly an alkylamine, alkyldiamine,  
19 alkylpolyamine, or an alkyleneamine, such as ethylene  
20 diamine, diethylenetriamine, triethylenetetramine,  
21 tetraethylenepentamine, and the like.

22  
23 Another class of nitrogen-containing compositions useful in  
24 preparing the molybdenum complexes employed in this  
25 invention includes the so-called dispersant viscosity index  
26 improvers (VI improvers). These VI improvers are commonly  
27 prepared by functionalizing a hydrocarbon polymer,  
28 especially a polymer derived from ethylene and/or propylene,  
29 optionally containing additional units derived from one or  
30 more co-monomers such as alicyclic or aliphatic olefins or  
31 diolefins. The functionalization may be carried out by a  
32 variety of processes which introduce a reactive site or  
33 sites which usually has at least one oxygen atom on the  
34 polymer. The polymer is then contacted with a

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01 nitrogen-containing source to introduce nitrogen-containing  
02 functional groups on the polymer backbone. Commonly used  
03 nitrogen sources include any basic nitrogen compound  
04 especially those nitrogen-containing compounds and  
05 compositions described herein. Preferred nitrogen sources  
06 are alkylene amines, such as ethylene amines, alkyl amines,  
07 and Mannich bases.  
08

09 Preferred basic nitrogen compounds for use in this invention  
10 are succinimides, carboxylic acid amides, and Mannich bases.  
11

12 Representative sulfur sources for preparing the molybdenum  
13 complexes used in this invention are sulfur, hydrogen  
14 sulfide, sulfur monochloride, sulfur dichloride, phosphorus  
15 pentasulfide,  $R_2S_x$  where R is hydrocarbyl, preferably  $C_{1-40}$   
16 alkyl, and x is at least 2, inorganic sulfides and  
17 polysulfides such as  $(NH_4)_2S_x$ , where x is at least 1,  
18 thioacetamide, thiourea, and mercaptans of the formula RSH  
19 where R is as defined above. Also useful as sulfurizing  
20 agents are traditional sulfur-containing antioxidants such  
21 as wax sulfides and polysulfides, sulfurized olefins,  
22 sulfurized carboxylic and esters and sulfurized  
23 ester-olefins, and sulfurized alkylphenols and the metal  
24 salts thereof.  
25

26 The sulfurized fatty acid esters are prepared by reacting  
27 sulfur, sulfur monochloride, and/or sulfur dichloride with  
28 an unsaturated fatty ester under elevated temperatures.  
29 Typical esters include  $C_1-C_{20}$  alkyl esters of  $C_8-C_{24}$   
30 unsaturated fatty acids, such as palmitoleic, oleic,  
31 ricinoleic, petroselinic, vaccenic, linoleic, linolenic,  
32 oleostearic, licanic, paranaric, tariric, gadoleic,  
33 arachidonic, cetoleic, etc. Particularly good results have  
34

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01 been obtained with mixed unsaturated fatty acid esters, such  
02 as are obtained from animal fats and vegetable oils, such as  
03 tall oil, linseed oil, olive oil, castor oil, peanut oil,  
04 rape oil, fish oil, sperm oil, and so forth.

05

06 Exemplary fatty esters include lauryl tallate, methyl  
07 oleate, ethyl oleate, lauryl oleate, cetyl oleate, cetyl  
08 linoleate, lauryl ricinoleate, oleyl linoleate, oleyl  
09 stearate, and alkyl glycerides.

10

11 Cross-sulfurized ester olefins, such as a sulfurized mixture  
12 of C<sub>10</sub>-C<sub>25</sub> olefins with fatty acid esters of C<sub>10</sub>-C<sub>25</sub> fatty  
13 acids and C<sub>1</sub>-C<sub>25</sub> alkyl or alkenyl alcohols, wherein the  
14 fatty acid and/or the alcohol is unsaturated may also be  
15 used.

16

17 Sulfurized olefins are prepared by the reaction of the C<sub>3</sub>-C<sub>6</sub>  
18 olefin or a low-molecular-weight polyolefin derived  
19 therefrom with a sulfur-containing compound such as sulfur,  
20 sulfur monochloride, and/or sulfur dichloride.

21

22 Also useful are the aromatic and alkyl sulfides, such as  
23 dibenzyl sulfide, dicyllyl sulfide, dicetyl sulfide,  
24 diparaffin wax sulfide and polysulfide, cracked wax-olefin  
25 sulfides and so forth. They can be prepared by treating the  
26 starting material, e.g., olefinically unsaturated compounds,  
27 with sulfur, sulfur monochloride, and sulfur dichloride.  
28 Particularly preferred are the paraffin wax thiomers  
29 described in U.S. Patent No. 2,346,156.

30

31 Sulfurized alkyl phenols and the metal salts thereof include  
32 compositions such as sulfurized dodecylphenol and the  
33 calcium salts thereof. The alkyl group ordinarily contains  
34

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01 from 9-300 carbon atoms. The metal salt may be preferably,  
02 a Group I or Group II salt, especially sodium, calcium,  
03 magnesium, or barium.

04

05 Preferred sulfur sources are sulfur, hydrogen sulfide,  
06 phosphorus pentasulfide,  $R_2S_x$  where R is hydrocarbyl,  
07 preferably  $C_1-C_{10}$  alkyl, and x is at least 3, mercaptans  
08 wherein R is  $C_1-C_{10}$  alkyl, inorganic sulfides and  
09 polysulfides, thioacetamide, and thiourea. Most preferred  
10 sulfur sources are sulfur, hydrogen sulfide, phosphorus  
11 pentasulfide, and inorganic sulfides and polysulfides.

12

13 The polar promoter used in the preparation of the molybdenum  
14 complexes employed in this invention is one which  
15 facilitates the interaction between the acidic molybdenum  
16 compound and the basic nitrogen compound. A wide variety of  
17 such promoters are well known to those skilled in the art.  
18 Typical promoters are 1,3-propanediol, 1,4-butane-diol,  
19 diethylene glycol, butyl cellosolve, propylene glycol,  
20 1,4-butyleneglycol, methyl carbitol, ethanolamine,  
21 diethanolamine, N-methyl-diethanol-amine, dimethyl  
22 formamide, N-methyl acetamide, dimethyl acetamide, methanol,  
23 ethylene glycol, dimethyl sulfoxide, hexamethyl  
24 phosphoramide, tetrahydrofuran and water. Preferred are  
25 water and ethylene glycol. Particularly preferred is water.

26

27 While ordinarily the polar promoter is separately added to  
28 the reaction mixture, it may also be present, particularly  
29 in the case of water, as a component of non-anhydrous  
30 starting materials or as waters of hydration in the acidic  
31 molybdenum compound, such as  $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$ . Water may  
32 also be added as ammonium hydroxide.

33

34



-15-

01 A method for preparing the molybdenum/sulfur complexes used  
02 in this invention is to prepare a solution of the acidic  
03 molybdenum precursor and a polar promoter with a basic  
04 nitrogen-containing compound with or without diluent. The  
05 diluent is used, if necessary, to provide a suitable  
06 viscosity for easy stirring. Typical diluents are  
07 lubricating oil and liquid compounds containing only carbon  
08 and hydrogen. If desired, ammonium hydroxide may also be  
09 added to the reaction mixture to provide a solution of  
10 ammonium molybdate. This reaction is carried out at a  
11 temperature from the melting point of the mixture to reflux  
12 temperature. It is ordinarily carried out at atmospheric  
13 pressure although higher or lower pressures may be used if  
14 desired. This reaction mixture is treated with a sulfur  
15 source as defined above at a suitable pressure and  
16 temperature for the sulfur source to react with the acidic  
17 molybdenum and basic nitrogen compounds. In some cases,  
18 removal of water from the reaction mixture may be desirable  
19 prior to completion of reaction with the sulfur source.

20  
21 In the reaction mixture, the ratio of molybdenum compound to  
22 basic nitrogen compound is not critical; however, as the  
23 amount of molybdenum with respect to basic nitrogen  
24 increases, the filtration of the product becomes more  
25 difficult. Since the molybdenum component probably  
26 oligomerizes, it is advantageous to add as much molybdenum  
27 as can easily be maintained in the composition. Usually,  
28 the reaction mixture will have charged to it from 0.01 to  
29 2.00 atoms of molybdenum per basic nitrogen atom.  
30 Preferably from 0.4 to 1.0, and most preferably from 0.4 to  
31 0.7, atoms of molybdenum per atom of basic nitrogen is added  
32 to the reaction mixture.

33

34

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01 The sulfur source is usually charged to the reaction mixture  
02 in such a ratio to provide 1.5 to 4.0 atoms of sulfur per  
03 atom of molybdenum. Preferably from 2.0 to 4.0 atoms of  
04 sulfur per atom of molybdenum is added, and most preferably,  
05 2.5 to 4.0 atoms of sulfur per atom of molybdenum.  
06

07 The polar promoter, which is preferably water, is ordinarily  
08 present in the ratio of 0.1 to 50 moles of promoter per mole  
09 of molybdenum. Preferably from 0.5 to 25 and most  
10 preferably 1.0 to 15 moles of the promoter is present per  
11 mole of molybdenum.  
12

13 As described above, the additive formulation employed in the  
14 present invention contains (1) a sulfurized  
15 molybdenum-containing composition, (2) a carboxylic acid  
16 amide, and (3) a succinimide.  
17

18 The carboxylic amide component of the presently employed  
19 additive formulation may be any of the carboxylic acid amide  
20 compounds described herein as useful in the preparation of  
21 the molybdenum/sulfur complex. Preferred carboxylic acid  
22 amide components include those amides derived from a  
23 carboxylic acid of the formula  $R^2\text{COOH}$ , wherein  $R^2$  is  $C_{12}$ - $C_{20}$   
24 alkyl, and an ethylene amine, such as triethylene tetramine  
25 or tetraethylene pentamine.  
26

27 Similarly, the succinimide component of the presently  
28 employed additive formulation may be any of the succinimide  
29 compounds described herein as useful in the preparation of  
30 the molybdenum/sulfur complex. Preferred succinimide  
31 components include those derived from polyisobutenyl  
32 succinic anhydride, wherein the polyisobutenyl group  
33 contains from about 50 to 250 carbon atoms, and an ethylene  
34

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01 amine, such as triethylene tetramine or tetraethylene  
02 pentamine.

03

04 The additive formulation employed in the present invention  
05 may additionally contain a flocculant inhibitor and/or a  
06 lubricity agent, such as a polyisobutene. If necessary, a  
07 diluent oil may also be included.

08

09 Other additives such as viscosity index improvers,  
10 antioxidants, dispersants, coupling agents, pour point  
11 depressants, extreme pressure agents, color stabilizers,  
12 rust inhibitors, anticorrosion agents, and the like, may  
13 also be present in the additive formulation.

14

15 The lubricant composition employed in the present invention  
16 comprises a major amount of a base oil of lubricating  
17 viscosity and a minor amount of the additive formulation  
18 described above.

19

20 The base oil employed may be any of a wide variety of oils  
21 of lubricating viscosity. Thus, the base oil can be a  
22 refined paraffin type base oil, a refined naphthenic base  
23 oil, or a synthetic hydrocarbon or non-hydrocarbon oil of  
24 lubricating viscosity. The base oil can also be a mixture  
25 of mineral and synthetic oils. For purposes of the present  
26 invention, the mineral lubricating oils are preferred, since  
27 they are presently in more general use in two-cycle engines.

28

29 The presently employed lubricant composition containing the  
30 additive formulation described herein can be conveniently  
31 prepared using conventional techniques by admixing the  
32 appropriate amount of each component of the additive  
33 formulation with a lubricating oil.

34

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01 Generally, the amount of the molybdenum-containing additive  
02 will vary from about 0.05 to 15% by weight and preferably  
03 from about 0.2 to 10% by weight, based on the total  
04 lubricant composition, including base oil. The carboxylic  
05 acid amide component will vary from about 0.05 to 20% by  
06 weight and preferably from about 0.2 to 15% by weight. The  
07 succinimide component will vary from about 0.5 to 15% by  
08 weight and preferably from about 0.2 to 10% by weight.  
09

10 The two-cycle engine fuel composition contemplated by the  
11 present invention comprises a major amount of fuel boiling  
12 in the gasoline range and minor amount of the lubricant  
13 composition disclosed herein.  
14

15 For purposes of the present invention, the lubricant  
16 composition will generally be added directly to the fuel to  
17 form a mixture of lubricant and fuel which is then  
18 introduced into the two-cycle engine cylinder. Generally,  
19 the resulting fuel composition will contain from about 15 to  
20 250 parts fuel per 1 part lubricant, and more typically  
21 about 50 to 100 parts fuel per 1 part lubricant. For some  
22 two-cycle engine applications, the lubricant may be directly  
23 injected into the combustion chamber along with the fuel or  
24 into the fuel just prior to the time the fuel enters the  
25 combustion chamber.  
26

27 The fuel employed in the present fuel composition is a  
28 hydrocarbon distillate fuel boiling in the gasoline range.  
29 In such gasoline fuels, other fuel additives may also be  
30 included such as antiknock agents, e.g.,  
31 methylcyclopentadienyl manganese tricarbonyl, tetramethyl or  
32 tetraethyl lead, or other dispersants or detergents such as  
33 various substituted amines, etc. Also included may be lead  
34 scavengers such as aryl halides, e.g., dichlorobenzene or

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01 alkyl halides, e.g., ethylene dibromide. Additionally,  
02 antioxidants, metal deactivators, pour point depressants,  
03 corrosion inhibitors and demulsifiers may be present.  
04

05 The following examples are presented to illustrate specific  
06 embodiments of this invention and are not to be construed in  
07 any way as limiting the scope of the invention.  
08

09 EXAMPLES

10  
11 Example 1

12  
13 To a 5000 ml flask was added 114 grams molybdenum trioxide  
14 and 196 grams of water. Stirring was started and 1200 grams  
15 of a solution of a 45% concentrate in oil of the  
16 polyisobutenyl succinimide prepared from polyisobutenyl  
17 succinic anhydride having a number average molecular weight  
18 for the polyisobutenyl group of about 950 and tetraethylene  
19 pentamine, and 1200 grams of hydrocarbon thinner were added.  
20 The mixture was refluxed at 100°C for 3 hours. The  
21 temperature was gradually increased over approximately  
22 1 hour to 170°C while distilling water. The temperature was  
23 maintained an additional hour after the water was removed.  
24 The temperature was lowered to 100°C-120°C and the mixture  
25 filtered and returned to the reaction vessel. To the  
26 solution was added 51 grams of sulfur. The mixture was  
27 heated to 160°C-180°C for 7 hours. The pressure was slowly  
28 reduced to about 50 mm of mercury to remove the hydrocarbon  
29 thinner. This produced 1244 grams of product containing  
30 1.80% nitrogen, 5.63% molybdenum, and 3.57% sulfur.  
31  
32  
33  
34

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01                                    Example 2

02

03    To a 5000 ml flask was added 52 grams molybdenum trioxide  
04    and 111 grams of water. Stirring was started and 1184 grams  
05    of a solution of a 45% concentrate in oil of the succinimide  
06    described in Example 1 and 1184 grams of hydrocarbon thinner  
07    were added. The mixture was refluxed at 100°C for 3 hours.  
08    The temperature was gradually increased over approximately  
09    1 hour to 170°C while distilling water. The temperature was  
10    maintained an additional hour after the water was removed.  
11    The temperature was lowered to 100°C-120°C and the mixture  
12    filtered and returned to the reaction vessel. To the  
13    solution was added 47 grams of sulfur. The mixture was  
14    heated to 160°C-180°C for 7 hours. The pressure was slowly  
15    reduced to about 50 mm of mercury to remove the hydrocarbon  
16    thinner. This produced 1220 grams of product containing  
17    1.94% nitrogen, 2.78% molybdenum, and 3.64% sulfur.

18

19                                    Example 3

20

21    To a 5000 ml flask was added 49 grams molybdenum trioxide  
22    and 105 grams of water. Stirring was started and 1133 grams  
23    of a solution of a 45% concentrate in oil of the succinimide  
24    described in Example 1 and 1133 grams of hydrocarbon thinner  
25    were added. The mixture was refluxed at 100°C for 3 hours.  
26    The temperature was gradually increased over approximately  
27    1 hour to 170°C while distilling water. The temperature was  
28    maintained an additional hour after the water was removed.  
29    The temperature was lowered to 100°C-120°C and the mixture  
30    filtered and returned to the reaction vessel. To the  
31    solution was added 22 grams of sulfur. The mixture was  
32    heated to 160°C-180°C for 7 hours. The pressure was slowly  
33    reduced to about 50 mm of mercury to remove the hydrocarbon

34

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01 thinner. This produced 1163 grams of product containing  
02 1.83% nitrogen, 2.79% molybdenum, and 1.97% sulfur.

03

04

Example 4

05

06 To a 5000 ml flask was added 1200 grams of a polyamide  
07 prepared from a C<sub>18</sub> carboxylic acid and tetraethylene  
08 pentamine and containing 6.4% nitrogen, 1200 grams  
09 hydrocarbon thinner, 42 grams molybdenum trioxide, and  
10 90 grams water. The mixture was refluxed at 100°C for  
11 3 hours. The temperature was gradually increased over  
12 approximately 1 hour to 170°C while distilling water. The  
13 temperature was maintained an additional hour after the  
14 water was removed. The temperature was lowered to  
15 100°C-120°C and the mixture filtered and returned to the  
16 reaction vessel. To the solution was added 21 grams of  
17 sulfur. The mixture was heated to 160°C-180°C for 7 hours.  
18 The pressure was slowly reduced to about 50 mm of mercury to  
19 remove the hydrocarbon thinner. This produced a product  
20 containing 5.88% nitrogen, 2.29% molybdenum, and 1.63%  
21 sulfur.

22

23

Example 5

24

25 The molybdenum/sulfur complexes of Examples 1, 2 and 4 were  
26 formulated to provide lubricant compositions containing 10%  
27 of the carboxylic acid amide reaction product of isostearic  
28 acid and tetraethylene pentamine, 2% of a polyisobutenyl  
29 succinimide prepared from polyisobutenyl succinic anhydride  
30 wherein the polyisobutenyl group has a number average  
31 molecular weight of about 950 and tetraethylene pentamine,  
32 2% of the molybdenum/sulfur complex of Examples 1, 2 and 4,  
33 respectively, 5% of a polyisobutene having a number average  
34

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01 molecular weight of about 950 as a lubricity agent, 0.5% of  
02 a flocculant inhibitor, 1% of a diluent oil and about 79.5%  
03 of a base oil. The base oil contains about 10% of a  
04 150 bright stock, about 70% of a mixture of 350N and 650N  
05 neutral oils, and about 20% of a petroleum distillate  
06 solvent.

07

08

Example 6

09

Two-Cycle Gasoline Engine Test

10

11 This test was used to evaluate the detergency and general  
12 performance of the fuel composition of this invention in a  
13 two-cycle water-cooled outboard engine. Piston varnish,  
14 ring sticking and general engine deposits were evaluated.

15

16 The test engine used was an Outboard Marine Company Johnson  
17 Model No. J70ELEIE outboard engine, which is a  
18 70 horsepower, water-cooled, three-cylinder, two-cycle  
19 engine.

20

21 The test procedure involved a two-hour break-in period,  
22 wherein the engine was run at 3,000 rpm for 1 hour, then at  
23 4,000 rpm for 1 hour, using a fuel:lubricant ratio of 50:1.

24

25 The test was then conducted for 98 hours using a 50:1 fuel  
26 to lubricant ratio on a 55 minute wide-open throttle,  
27 5 minute idle cycle. The total test time, including  
28 break-in, was 100 hours.

29

30 At the conclusion of the test, the engine was disassembled  
31 and rated. The average piston rating and average  
32 second-ring sticking rating for 3 cylinders was measured.  
33 In the rating system employed, the higher the numerical  
34 rating, the better the cleanliness performance, with 10.0



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01 being the maximum rating. Except for the piston rings, the  
02 ratings are for cleanliness. The piston rings are rated for  
03 the degree of sticking, with a rating of 10.0 indicating a  
04 completely free piston ring.

05

06 The second-ring sticking values include a National Marine  
07 Manufacturers Association (NMMA) rating, a visual rating,  
08 and an adjusted rating, which is an average of the NMMA and  
09 visual ratings.

10

11 The reference oil employed in this test was NMMA reference  
12 oil TCW II, used as an industry standard in two-cycle engine  
13 tests to measure engine cleanliness. The TCW II reference  
14 oil is a standard mineral lubricating oil containing a  
15 commercial ashless dispersant for gasoline two-cycle  
16 engines. The reference oil is available from Citgo  
17 Petroleum Corporation, Tulsa, Oklahoma.

18

19 Engine test runs were performed with a 50:1 fuel to  
20 lubricant ratio, using lubricant compositions containing the  
21 molybdenum/sulfur complexes of Examples 1, 2 and 4,  
22 formulated as described in Example 5. The results of the  
23 engine tests are shown in Table 1.

24

25 The results shown in Table 1 demonstrate that the fuel  
26 composition of the present invention is highly effective in  
27 reducing piston deposits and piston ring sticking in  
28 two-cycle engines, and generally exceeds the performance of  
29 a fuel containing the industry standard reference oil.

30

31

32

33

34

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TABLE 1							
TWO-CYCLE ENGINE TEST RESULTS							
Average Rating for 3 Cylinders							
Additive	Piston Skirt	Crown	2-Ring Land	Under-Crown	Second-Ring Sticking		
					NMMA	Visual	Adj.
TCW II Reference Oil	7.1	2.8	3.7	2.8	6.8	5.7	6.3
Example 1 <sup>(a)</sup>	7.4	3.4	4.4	2.5	7.1	6.1	6.6
Example 4 <sup>(a)</sup>	7.7	3.1	4.8	3.9	7.8	6.8	7.3
Example 2 <sup>(a)</sup>	7.8	3.4	4.4	3.3	8.5	6.5	7.5

<sup>(a)</sup>Formulated as in Example 5.

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01 WHAT IS CLAIMED IS:

02

03 1. A fuel composition for two-cycle engines comprising a  
04 major amount of fuel boiling in the gasoline range and  
05 a minor amount of a lubricant composition comprising:

06

07 (A) a major amount of a base oil of lubricating  
08 viscosity, and

09

10 (B) a minor amount of an additive formulation  
11 comprising:

12

13 (1) a sulfurized molybdenum-containing  
14 composition prepared by (i) reacting an  
15 acidic molybdenum compound and a basic  
16 nitrogen compound selected from the group  
17 consisting of a succinimide, a carboxylic  
18 acid amide, a hydrocarbyl monoamine, a  
19 hydrocarbyl polyamine, a Mannich base, a  
20 phosphoramidate, a thiophosphoramidate, a  
21 phosphonamide, a dispersant viscosity index  
22 improver, or a mixture thereof, in the  
23 presence of a polar promoter, to form a  
24 molybdenum complex wherein from 0.01 to  
25 2 atoms of molybdenum are present per basic  
26 nitrogen atom, and the promoter is present in  
27 the ratio of 0.01 to 50 moles of polar  
28 promoter per mole of molybdenum; and  
29 (ii) reacting the molybdenum complex with a  
30 sulfur-containing compound in an amount  
31 sufficient to provide about 1.5 to 4.0 atoms  
32 of sulfur per atom of molybdenum, to thereby  
33 form a sulfur- and molybdenum-containing  
34 composition,

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- 01                   (2) a carboxylic acid amide, and  
02  
03                   (3) a succinimide.  
04
- 05       2. The fuel composition of Claim 1, wherein the sulfur  
06       source for component (1) is sulfur, hydrogen sulfide,  
07       phosphorus pentasulfide,  $R_2S_x$  where R is hydrocarbyl,  
08       and x is at least 2, inorganic sulfides or inorganic  
09       polysulfides, thioacetamide, thiourea, mercaptans of  
10       the formula RSH where R is hydrocarbyl, or a  
11       sulfur-containing antioxidant.  
12
- 13       3. The fuel composition of Claim 2, wherein the sulfur  
14       source for component (1) is sulfur, hydrogen sulfide,  
15       phosphorus pentasulfide,  $R_2S_x$  where R is  $C_{1-4}$   
16       hydrocarbyl, and x is at least 3, inorganic sulfides,  
17       or inorganic polysulfides, thioacetamide, thiourea or  
18       RSH where R is  $C_{1-40}$  alkyl, and the acidic molybdenum  
19       compound is molybdic acid, ammonium molybdate, or  
20       alkali metal molybdate.  
21
- 22       4. The fuel composition of Claim 3, wherein said sulfur  
23       source is sulfur, hydrogen sulfide, RSH where R is  $C_{1-10}$   
24       alkyl, phosphorus pentasulfide, or  $(NH_4)_2S_{x'}$ , where x'  
25       is at least 1, said acidic molybdenum compound is  
26       molybdic acid, or ammonium molybdate, and said basic  
27       nitrogen compound is a succinimide, carboxylic acid  
28       amide, or Mannich base.  
29
- 30       5. The fuel composition of Claim 4, wherein said basic  
31       nitrogen compound is a  $C_{24-350}$  hydrocarbyl succinimide,  
32       carboxylic acid amide, or a Mannich base prepared from  
33       a  $C_{9-200}$  alkylphenol, formaldehyde, and an amine.  
34

- 01 6. The fuel composition of Claim 5, wherein said basic  
02 nitrogen compound is a polyisobutenyl succinimide  
03 prepared from polyisobutenyl succinic anhydride and  
04 tetraethylene pentamine or triethylene tetramine.  
05
- 06 7. The fuel composition of Claim 5, wherein said basic  
07 nitrogen compound is a carboxylic acid amide prepared  
08 from one or more carboxylic acids of the formula  
09  $R^2\text{COOH}$ , or a derivative thereof which upon reaction  
10 with an amine yields a carboxylic acid amide, wherein  
11  $R^2$  is  $C_{12-350}$  alkyl or  $C_{12-350}$  alkenyl and a hydrocarbyl  
12 polyamine.  
13
- 14 8. The fuel composition of Claim 7, wherein  $R^2$  is  $C_{12-20}$   
15 alkyl or  $C_{12-20}$  alkenyl and the hydrocarbyl polyamine is  
16 tetraethylene pentamine or triethylene tetramine.  
17
- 18 9. The fuel composition of Claim 5, wherein said basic  
19 nitrogen compound is a Mannich base prepared from  
20 dodecylphenol, formaldehyde, and methylamine.  
21
- 22 10. The fuel composition of Claim 5, wherein said basic  
23 nitrogen compound is a Mannich base prepared from  
24  $C_{80-100}$  alkylphenol, formaldehyde and triethylene  
25 tetramine, tetraethylene pentamine, or mixtures  
26 thereof.  
27
- 28 11. The fuel composition of Claim 1, wherein the polar  
29 promoter is water.  
30
- 31 12. The fuel composition of Claim 1, wherein the carboxylic  
32 acid amide of component (2) is derived from a  
33  
34

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- 01 carboxylic acid of the formula  $R^2\text{COOH}$ , wherein  $R^2$  is  
02  $\text{C}_{12-20}$  alkyl, and an ethylene amine.  
03
- 04 13. The fuel composition of Claim 1, wherein the  
05 succinimide of component (3) is derived from  
06 polyisobutenyl succinic anhydride, wherein the  
07 polyisobutenyl group contains from about 50 to  
08 250 carbon atoms, and an ethylene amine.  
09
- 10 14. The fuel composition of Claim 1, wherein the lubricant  
11 composition contains about 0.05 to 15% by weight of the  
12 molybdenum-containing composition of component (1),  
13 about 0.05 to 20% by weight of the carboxylic acid  
14 amide of component (2), and about 0.05 to 15% by weight  
15 of the succinimide of component (3).  
16
- 17 15. The fuel composition of Claim 1, wherein the molybdenum  
18 complex is reacted with the sulfur-containing compound  
19 in an amount sufficient to provide about 2.0 to  
20 4.0 atoms of sulfur per atom of molybdenum.  
21
- 22 16. The fuel composition of Claim 15, wherein the  
23 molybdenum complex is reacted with the  
24 sulfur-containing compound in an amount sufficient to  
25 provide about 2.5 to 4.0 atoms of sulfur per atom of  
26 molybdenum.  
27
- 28 17. The fuel composition of Claim 1, wherein the additive  
29 formulation further contains a flocculant inhibitor.  
30
- 31 18. The fuel composition of Claim 17, wherein the additive  
32 formulation further contains a lubricity agent.  
33  
34

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- 01 19. A method for reducing engine deposits and piston ring  
02 sticking in a two-cycle engine which comprises  
03 operating the two-cycle engine with a fuel composition  
04 comprising a major amount of fuel boiling in the  
05 gasoline range and a minor amount of a lubricant  
06 composition comprising:  
07
- 08 (A) a major amount of a base oil of lubricating  
09 viscosity, and  
10
- 11 (B) a minor amount effective to reduce engine deposits  
12 and piston ring sticking of an additive  
13 formulation comprising:  
14
- 15 (1) a sulfurized molybdenum-containing  
16 composition prepared by (i) reacting an  
17 acidic molybdenum compound and a basic  
18 nitrogen compound selected from the group  
19 consisting of a succinimide, a carboxylic  
20 acid amide, a hydrocarbyl monoamine, a  
21 hydrocarbyl polyamine, a Mannich base, a  
22 phosphoramidate, a thiophosphoramidate, a  
23 phosphonamide, a dispersant viscosity index  
24 improver, or a mixture thereof, in the  
25 presence of a polar promoter, to form a  
26 molybdenum complex wherein from 0.01 to  
27 2 atoms of molybdenum are present per basic  
28 nitrogen atom, and the promoter is present in  
29 the ratio of 0.01 to 50 moles of polar  
30 promoter per mole of molybdenum; and  
31 (ii) reacting the molybdenum complex with a  
32 sulfur-containing compound in an amount  
33 sufficient to provide about 1.5 to 4.0 atoms  
34 of sulfur per atom of molybdenum, to thereby

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01 form a sulfur- and molybdenum-containing  
02 composition;

03

04 (2) a carboxylic acid amide; and

05

06 (3) a succinimide.

07

08 20. The method of Claim 19 wherein the sulfur source for  
09 component (1) is sulfur, hydrogen sulfide, phosphorus  
10 pentasulfide,  $R_2S_x$  where R is hydrocarbyl, and x is at  
11 least 2, inorganic sulfides or inorganic polysulfides,  
12 thioacetamide, thiourea, mercaptans of the formula RSH  
13 where R is hydrocarbyl, or a sulfur-containing  
14 antioxidant.

15

16 21. The method of Claim 20 wherein the sulfur source for  
17 component (1) is sulfur, hydrogen sulfide, phosphorus  
18 pentasulfide,  $R_2S_x$  where R is  $C_{1-4}$  hydrocarbyl, and x is  
19 at least 3, inorganic sulfides, or inorganic  
20 polysulfides, thioacetamide, thiourea or RSH where R is  
21  $C_{1-40}$  alkyl, and the acidic molybdenum compound is  
22 molybdic acid, ammonium molybdate, or alkali metal  
23 molybdate.

24

25 22. The method of Claim 21 wherein said sulfur source is  
26 sulfur, hydrogen sulfide, RSH where R is  $C_{1-10}$  alkyl,  
27 phosphorus pentasulfide, or  $(NH_4)_2S_{x'}$ , where  $x'$  is at  
28 least 1, said acidic molybdenum compound is molybdic  
29 acid, or ammonium molybdate, and said basic nitrogen  
30 compound is a succinimide, carboxylic acid amide, or  
31 Mannich base.

32

33

34



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- 01 23. The method of Claim 22 wherein said basic nitrogen  
02 compound is a C<sub>24-350</sub> hydrocarbyl succinimide,  
03 carboxylic acid amide, or a Mannich base prepared from  
04 a C<sub>9-200</sub> alkylphenol, formaldehyde, and an amine.  
05
- 06 24. The method of Claim 23 wherein said basic nitrogen  
07 compound is a polyisobutenyl succinimide prepared from  
08 polyisobutenyl succinic anhydride and tetraethylene  
09 pentamine or triethylene tetramine.  
10
- 11 25. The method of Claim 23 wherein said basic nitrogen  
12 compound is a carboxylic acid amide prepared from one  
13 or more carboxylic acids of the formula R<sup>2</sup>COOH, or a  
14 derivative thereof which upon reaction with an amine  
15 yields a carboxylic acid amide, wherein R<sup>2</sup> is C<sub>12-350</sub>  
16 alkyl or C<sub>12-350</sub> alkenyl and a hydrocarbyl polyamine.  
17
- 18 26. The method of Claim 25 wherein R<sup>2</sup> is C<sub>12-20</sub> alkyl or  
19 C<sub>12-20</sub> alkenyl and the hydrocarbyl polyamine is  
20 tetraethylene pentamine or triethylene tetramine.  
21
- 22 27. The method of Claim 23 wherein said basic nitrogen  
23 compound is a Mannich base prepared from dodecylphenol,  
24 formaldehyde, and methylamine.  
25
- 26 28. The method of Claim 23 wherein said basic nitrogen  
27 compound is a Mannich base prepared from C<sub>80-100</sub>  
28 alkylphenol, formaldehyde and triethylene tetramine,  
29 tetraethylene pentamine, or mixtures thereof.  
30
- 31 29. The method of Claim 19 wherein the polar promoter is  
32 water.  
33  
34

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- 01 30. The method of Claim 19 wherein the carboxylic acid  
02 amide of component (2) is derived from a carboxylic  
03 acid of the formula  $R^2\text{COOH}$ , wherein  $R^2$  is  $\text{C}_{12-20}$  alkyl,  
04 and an ethylene amine.  
05
- 06 31. The method of Claim 19 wherein the succinimide of  
07 component (3) is derived from polyisobutenyl succinic  
08 anhydride, wherein the polyisobutenyl group contains  
09 from about 50 to 250 carbon atoms, and an ethylene  
10 amine.  
11
- 12 32. The method of Claim 19 wherein the lubricant  
13 composition contains about 0.05 to 15% by weight of the  
14 molybdenum-containing composition of component (1),  
15 about 0.05 to 20% by weight of the carboxylic acid  
16 amide of component (2), and about 0.05 to 15% by weight  
17 of the succinimide of component (3).  
18
- 19 33. The method of Claim 19 wherein the molybdenum complex  
20 is reacted with the sulfur-containing compound in an  
21 amount sufficient to provide about 2.0 to 4.0 atoms of  
22 sulfur per atom of molybdenum.  
23
- 24 34. The method of Claim 33 wherein the molybdenum complex  
25 is reacted with the sulfur-containing compound in an  
26 amount sufficient to provide about 2.5 to 4.0 atoms of  
27 sulfur per atom of molybdenum.  
28
- 29 35. The method of Claim 19 wherein the additive formulation  
30 further contains a flocculant inhibitor.  
31
- 32 36. The method of Claim 35 wherein the additive formulation  
33 further contains a lubricity agent.  
34

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/08471

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>																				
IPC(5) : C10M 159/18, 133/16, 149/00 US CL : 252/42.7, 46.4, 51.5A According to International Patent Classification (IPC) or to both national classification and IPC																				
<b>B. FIELDS SEARCHED</b>																				
Minimum documentation searched (classification system followed by classification symbols) U.S. : 252/42.7, 46.4, 51.5A, 44/367, 330,331																				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
Y	US, A, 4,263,152 (King et al) 21 April 1981, see col. 2, lines 10 et seq. and col. 7, lines 5-47.	1-36																		
Y	US, A, 3,405,064 (Miller) 08 October 1968, see col. 1, lines 19-40 and lines 55 et seq.	1-36																		
Y	US, A, 3,219,666 (Norman et al) 23 November 1965, see entire document.	1-36																		
A	US, A, 4,266,945 (Karn) 12 May 1981, see entire document.	1-36																		
A	US, A, 4,164,473 (Coupland et al) 14 August 1979, see entire document.	1-36																		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
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*O* document referring to an oral disclosure, use, exhibition or other means																				
*P* document published prior to the international filing date but later than the priority date claimed																				
Date of the actual completion of the international search 19 NOVEMBER 1993		Date of mailing of the international search report 05 JAN 1994																		
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